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(54) Title: CONTROLLED FREE RADICAL POLYMERIZATION PROCESS

(57) Abstract

A polymerization process for the preparation of (meth)acrylate containing homopolymers or block copolymers comprises heating a mixture of a free radical initiator, a stable free radical agent, and a polymerizable monomer compound to form a thermoplastic resin or resins with a narrow polydispersity. The stable free radical agent is a piperazinone or morpholone based nitroxide or any adducts thereof.

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CONTROLLED FREE RADICAL POLYMERIZATION PROCESS

Background of the Invention

1. FIELD OF THE INVENTION

This invention relates to the application of new
nitroxides in the controlled free radical
polymerization of a thermoplastic resin or resins.
More particularly, the invention relates to a
controlled free radical polymerization process wherein
piperazinone and morpholone based nitroxides as well
as their adducts are used to provide styrene and
(meth)acrylate homopolymers and block copolymer resin
products characterized by high monomer to polymer
conversion and possessing narrow polydispersity
properties.

2. DESCRIPTION OF THE PRIOR ART

Stable Free Radical Polymerization (SFRP) refers
to a free radical polymerization in the presence of a
stable free radical such as a nitroxide. The
nitroxide traps carbon-centered radicals to form
adducts. The trapping is reversible but the
equilibrium is such that most (99%) polymer chains are
dormant and only a very small fraction is dissociated.
Thus, the concentration of free radicals is

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effectively lowered at all times in the polymerization
as shown below, wherein P• represents the growing
polymer radical, •ON represents the nitroxide, and M
represents a monomer.

$$P_n\text{-ON} \rightleftharpoons^K P_n\bullet \ + \ \bullet ON$$

$$\downarrow \text{propagation}$$

$$M$$

$$P_{n+1}\text{-ON} \rightleftharpoons^K P_{n+1}\bullet \ \downarrow \ \bullet ON$$
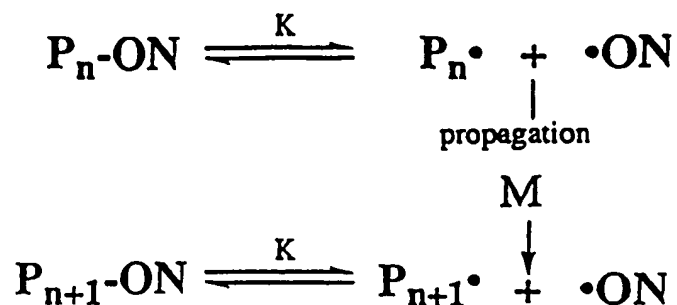
This in turn affects propagation and transfer rates
but has an even greater effect on termination, since
the latter is second order in radical concentration.

Thus, stable free radical polymerization
minimizes chain termination reactions, while improving
molecular weight and polymer architecture control. On
the other hand, the SFRP technology slows down the
polymerization process.

In United States Letters Patent No. 5,412,047,
issued May 2, 1995 to Georges, et al., processes for
the preparation of homopolymers of (meth)acrylic
monomers and copolymers containing (meth)acrylate
segments by nitroxide mediated polymerization are
shown. The polymerization process comprises heating a
mixture of a free radical initiator and an oxo-
nitroxide, specifically 4-oxo-TEMPO (4-oxo-2,2,6,6-
tetramethyl-1-piperidinyloxy), as a stable free

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radical agent, at least one polymerizable

(meth)acrylate monomer compound, and optionally a

solvent, to form a homopolymeric (meth)acrylate

containing thermoplastic resin or resins with a high

5   monomer to polymer conversion and a narrow

polydispersity.

        Examples of other stable free radical compounds

said to be suitable for use in the '047 Patent

include: 2,2,6,6-tetramethyl-1-piperidinyloxy free

10   radical (TEMPO); 4-hydroxy-2,2,6,6-tetramethyl-1-

piperidinyloxy free radical; 2,2,5,5-tetramethyl-1-

pyrrolidinyloxy; 3-carboxy-2,2,5,5-tetramethyl-1

pyrrolidinyloxy; and ditert-butyl nitroxide. As noted

in the '047 Patent, though, surprisingly and

15   unexpectedly, the aforementioned stable free radical

compounds, and related derivatives, while said to be

quite satisfactory for the purpose of moderating the

polymerization of a wide variety of different monomer

types and comonomers, are completely ineffective when

20   used in homopolymerizations of (meth)acrylate

monomers. That is to say, no homopolymeric product

formation could be detected by GPC when a mixture of

n-butyl acrylate, a free radical initiator such as

benzoyl peroxide or AIBN, and a stable free radical

25   compound of the type listed in the '047 Patent were

heated for about 10 hours at about 140°C.

        A solution to the problem of forming

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(meth)acrylate copolymers and copolymers was said to
be achieved in the '047 Patent by substituting, for
example, the carbonyl containing stable free radical
4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxy (4-oxo-
5   TEMPO) in place of the aforementioned ineffective
stable free radical compounds. However, 4-oxo-TEMPO
is not a stable free radical when heated above 100°C
in the presence of carbon radicals. Under these
conditions it is known by those skilled in the art
10   that 4-oxo-TEMPO decomposes rapidly to phorone and
other non-radical compounds as set out in Volodarsky,
L.B. et al., "Synthetic Chemistry of Stable
Nitroxides", p. 50 (CRC Press 1993) and Yoshioka, T.,
Higa Shida, S., Morimura, S., and Murayama, K., 44
15   Bull. Chem. Soc. Jpn., Volume 44, pp. 2207-2210
(1971).

        All nitroxides based on TEMPO and its derivatives
and used by the inventors of the '047 Patent,
including 4-oxo-TEMPO, are problematic, particularly
20   when used in the synthesis of (meth)acrylate
homopolymers, styrene-n-butyl acrylate block
copolymers, and n-butyl acrylate-styrene block
copolymers, in that the polymers can not be
synthesized in a controlled fashion with high yields.
25   Further, these nitroxides are undesirable for various
practical reasons — that is, the nitroxides cannot be
synthetically modified easily. Nor do the nitroxides

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have a long shelf-life.

Thus, there remains a need for a controlled free radical polymerization process, which can be used to simply and economically synthesize high yields of (meth)acrylate homopolymers as well as styrene-n-butyl acrylate or n-butylacrylate-styrene block copolymers. In this regard, a need also exists for a stable free radical nitroxide for use in the polymerization process, which can be easily synthesized and stored over long periods of time.

Incorporation by Reference

U.S. Patent Nos. 5,412,047, 4,914,232, 4,466,915, 5,401,804, and 4,581,429 are incorporated by reference herein as background information with respect to the present invention.

Brief Summary of the Invention

We have discovered that piperazinone and morpholone based nitroxides as well as their adducts can be used in the (meth)acrylate polymerization processes of the '047 Patent with unexpectedly high efficiencies. These nitroxides are advantageous in that they are easily synthesized, particularly with regard to tailoring the nitroxide structure to improve reaction rates, introduce functionality, and tailor solubility. Further, these nitroxides have an

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improved shelf-life stability, since they are highly
crystalline and can be stored indefinitely at room
temperature or higher.

In addition, these nitroxides, quite
5   unexpectedly, can be used to efficiently make high
yields of styrene-*n*-butyl acrylate or *n*-butyl
acrylate-styrene block copolymers with narrow
polydispersities (1.0-3.0) simply and economically,
while controlling both molecular weight and
10   composition. Indeed, when used in the preparation of
these styrene-block-acrylate copolymers, high yields
of styrene or (meth)acrylate prepolymer are obtained
in the first step of the polymerization process, thus
enabling high yields of the styrene-block-
15   (meth)acrylate copolymers in the second step of the
polymerization process.

Block copolymers made in the presence of stable
free radicals have been claimed in U.S. Patent Nos.
5,322,912, 5,401,804, 5,449,998 and 5,545,504 but have
20   only been reduced to practice for a styrene-styrene
sulfonate diblock copolymer. We have found that
(meth)acrylate containing block copolymers cannot be
made using the nitroxides claimed in the
aforementioned patents.

25   In addition, use of our nitroxides for styrene or
(meth)acrylate homopolymerization showed a distinct
rate advantage over TEMPO and its derivatives.

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The present invention, then, provides an improvement in the process for the stable free radical polymerization by using new nitroxides to make homopolymers of (meth)acrylate monomers and copolymers containing (meth)acrylate segments by nitroxide mediated polymerization.

According to a first aspect of the invention, a free radical polymerization process for the preparation of a thermoplastic resin or resins is disclosed, which comprises heating from about 80°C to about 160°C a mixture of a free radical initiator, at least one polymerizable monomer compound, and a stable free radical agent comprising a nitroxyl radical to form the thermoplastic resin or resins having a polydispersity from about 1.0 to about 3.0. The nitroxyl radical has the following formula:
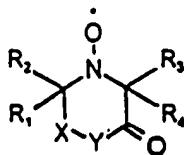
$$
\begin{array}{c}
\overset{\displaystyle \cdot}{\underset{}{O}}\\[2pt]
R_2\underset{R_1}{\diagup}\!\!\overset{}{\underset{}{N}}\!\!\underset{R_4}{\diagdown}R_3\\[2pt]
X\!\!-\!\!Y\overset{}{\underset{O}{}}
\end{array}
$$

wherein X is CH_2 or $C=O$, Y is O or $N-R$, R, R_1, R_2, R_3, and R_4 are independently selected from the group consisting of aryl, alkyl having from 1 to about 24 carbon atoms, cycloalkyl having from 5 to about 7 carbon atoms, aralkyl having from 7 to about 20 carbon atoms, cyanoalkyl having from 2 to about 12 carbon

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atoms, ether having from 4 to about 18 carbon atoms,
and hydroxyalkyl having from 1 to about 18 carbon
atoms; and

R_1 and R_2 together, or R_3 and R_4 together, or each
pair, may be cyclized forming a ring having from about
5 to about 14 carbon atoms.

According to a second aspect of the present
invention, a free radical polymerization process for
the preparation of a thermoplastic resin or resins is
disclosed, which comprises heating from about 80°C to
about 160°C a mixture of at least one polymerizable
monomer compound, and a preformed nitroxide adduct to
form the thermoplastic resin or resins. The preformed
nitroxide adduct has the following formula:

wherein X is CH_2 or $C=O$, Y is O or N-R, R, R_1, R_2, R_3,
R_4, and R_5 are independently selected from the group
consisting of aryl, alkyl having from 1 to about 24
carbon atoms, cycloalkyl having from 5 to about 7
carbon atoms, aralkyl having from 7 to about 20 carbon
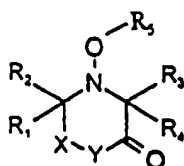atoms, cyanoalkyl having from 2 to about 12 carbon
atoms, ether having from 4 to about 18 carbon atoms,
and hydroxyalkyl having from 1 to about 18 carbon

atoms; and

R$_1$ and R$_2$ together, or R$_3$ and R$_4$ together, or each pair, may be cyclized forming a ring having from about 5 to about 14 carbon atoms.

5   According to a third aspect of the invention, a free radical polymerization process for the preparation of a (meth)acrylate containing block copolymer is closed. In the first step, a first mixture of either (1) a free radical initiator; a 10   first polymerizable monomer compound; and a stable free radical agent comprising the nitroxide radical having the formula disclosed above; or (2) a first polymerizable monomer compound and a preformed nitroxide adduct having the formula disclosed above is 15   heated from about 80°C to about 160°C to form a prepolymer. In the second step, a second mixture containing the prepolymer and the second polymerizable compound is heated from about 80°C to about 60°C, the second polymerizable monomer compound being different 20   than the first polymerizable monomer compound.

One advantage of the present invention is that a new nitroxide useful in the controlled free radical polymerization of a thermoplastic resin or resins can be easily synthesized, particularly with regard to 25   tailoring the nitroxide structure to improve reaction rates, introduce functionality, tailor solubility, etc.

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Another advantage of the present invention is that a new nitroxide useful in the controlled radical polymerization of a thermoplastic resin or resins has an improved shelf-life stability. The new nitroxides

5   are highly crystalline and can be stored indefinitely at room temperature (or higher), which cannot be said for TEMPO and its derivatives.

Still another advantage of the present invention is that a controlled radical polymerization process is

10   disclosed wherein styrene can be polymerized at a faster rate.

Still another advantage of the present invention is that a controlled free radical polymerization process is disclosed wherein higher conversions in

15   styrene and (meth)acrylate are achieved.

Still another advantage of the present invention is that styrene-block-acrylate copolymers can be synthesized using a controlled free radical polymerization process wherein high yields of a

20   styrene or (meth)acrylate prepolymer are obtained in the first step of the polymerization process, thus enabling high yields of the styrene-block-(meth)acrylate copolymers in the second step of the polymerization process.

25   Still another advantage of the present invention is that a controlled radical polymerization process is disclosed wherein styrene-nBA block copolymers can be

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simply and economically synthesized.

Still another advantage of the present invention
is that a controlled radical polymerization process is
disclosed wherein nBA-styrene block copolymers can be

5   simply and economically synthesized.

Still other benefits and advantages of the
invention will become apparent to those skilled in the
art upon a reading and understanding of the following
detailed specification.

10

Detailed Description of the Preferred Embodiment

The present invention provides (meth)acrylate
polymerization processes for preparing (meth)acrylate
containing polymeric resins with well-defined

15   molecular weight properties and narrow
polydispersities.

The processes can be run as batch, semi-
continuous or continuous processes. The
polymerization process for the preparation of

20   (meth)acrylate containing resins is initiated using a
classical free radical initiator in the presence of a
slight excess of free nitroxide and comprises heating
a mixture comprised of a free radical initiator, a
stable free radical agent, at least one polymerizable

25   (meth)acrylate monomer compound, and optionally a
solvent, to form a (meth)acrylate containing resin
with a high monomer to polymer conversion and a narrow

polydispersity. As used in the present specification,
the terminology "(meth)acrylate containing" means that
about 5 to 100 wt.% of the total monomer polymerized
is a (meth)acrylate type monomer and that the

5   (meth)acrylate monomer is polymerized in the presence
of the stable free radical compound or nitroxide
containing prepolymers.

       Suitable for use as free radical initiators in
the processes of the present invention include any

10   conventional free radical initiators known in the art.
These initiators can include oxygen, hydroperoxides,
peresters, percarbonates, peroxides, persulfates and
azo initiators. Specific examples of some suitable
initiators include hydrogen peroxide, t-butyl

15   hydroperoxide, ditertiary butyl peroxide, tertiary-
amyl hydroperoxide, dibenzoyl peroxide (AIBN),
potassium persulfate, and methylethyl ketone peroxide.
The initiators are normally used in amounts of from
about 0.01% to about 4% based on the weight of total

20   polymerizable monomer. A preferred range is from
about 0.05% to about 2% by weight of the total
polymerizable monomer.

       Redox initiators may also be used in the practice
of the present invention and include sodium bisulfite,

25   sodium sulfite, isoascorbic acid, sodium formaldehyde-
sulfoxylate, and the like, used with suitable
oxidizing agents, such as the thermal initiators noted

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above. If used, the redox initiators may be used in amounts of 0.001% to 5%, based on the weight of total monomer. A preferred range is from about 0.01% to about 3% by weight of total polymerizable monomer.

5   The stable free radical selected for use in the present invention are piperazinone and morpholone based nitroxides and their adducts. These nitroxides are critical to the success of the stable free radical polymerization process disclosed in the present

10   invention. For example, controlled nitroxide mediated polymerization of n-butyl acrylate has not been reported in the prior art. The process described in the '047 Patent, wherein TEMPO and its derivatives are used as the nitroxide stable free radical agent, can

15   only be controlled at very low conversions — that is, less than 15%.

           In particular, the piperazinonyl nitroxides compare favorably to 4-oxo-TEMPO in the homopolymerization of n-butyl acrylate. Indeed, a

20   comparison of our iBu nitroxide (TABLE I) and our C7 nitroxide (TABLE I) versus 4-oxo-TEMPO in a high temperature polymerization demonstrates large differences in the obtained yields and molecular weights as shown in Examples 13 and 14 and Comparative

25   Example 2.

           The synthesis of the piperazinone based nitroxides is shown below in Equation (1). An

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alternative morpholone based nitroxide, is shown in
reaction (2), which uses a much more readily available
amino alcohol starting material. The nitroxides are
obtained in high yields by either method.

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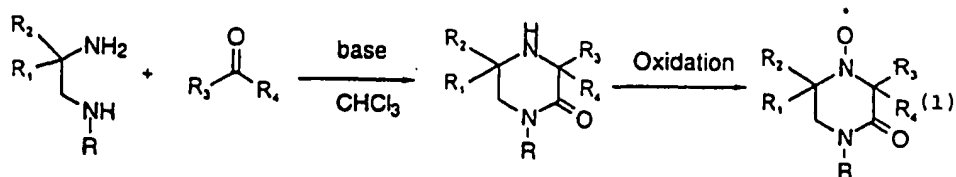
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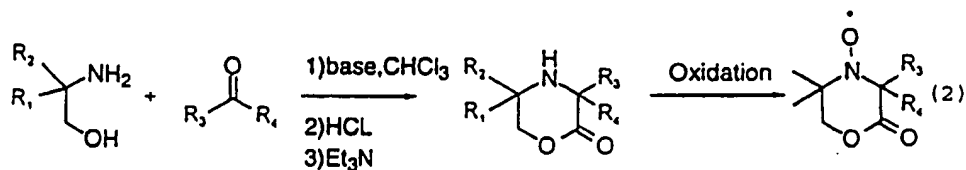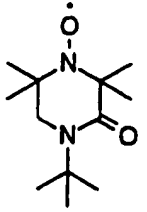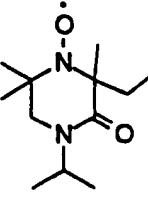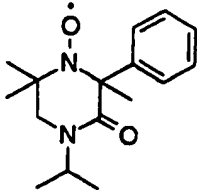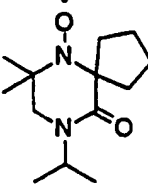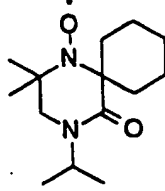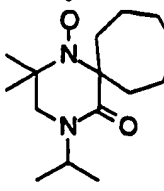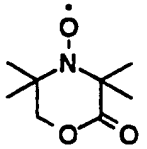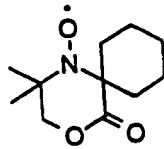
15   Certain piperazinone based nitroxides and
morpholone based nitroxides obtained and used in the
practice of the present invention, including their
abbreviations, are listed below in **TABLE I**. The
nomenclature adopted reflects the nature of the

20   substituents introduced via the ketone.
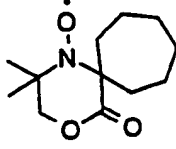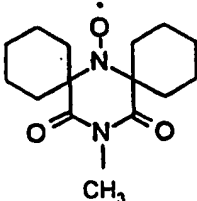
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TABLE I

NITROXIDE STRUCTURE	ABBREVIATION	NITROXIDE STRUCTURE	ABBREVIATION
	Dimethyl (1-tertbutyl-3,3,5,5-tetramethyl-2-piperazinone-oxide)		iBu (3-isobutyl-1-isopropyl-3,5,5-trimethyl-2-piperazinone-oxide)
	Phenyl (1-isopropyl-3-phenyl-3,5,5-trimethyl-2-piperazinone-oxide)		C5 (3,3-tetramethylene-5,5-dimethyl-1-isopropyl-2-piperazinone-oxide)
	C6 (3,3-pentamethylene-5,5-dimethyl-1-isopropyl-2-piperazinone-oxide)		C7 (3,3-hexamethylene-5,5-dimethyl-1-isopropyl-2-piperazinone-oxide)
	diMe Morpholone (3,3,5,5-tetramethyl-2-morpholone-oxide)		C6 Morpholone (3,3-pentamethylene-5,5-dimethyl-2-morpholone-oxide)

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NITROXIDE STRUCTURE	ABBREVIATION	NITROXIDE STRUCTURE	ABBREVIATION
	C7 Morpholone (3,3-hexamethylene-5,5-dimethyl-2-morpholone oxide)		Dicyclohexyl (bis-3,3,5,5-pentamethylene-2,6-piperazinone-dione-oxide)

One class of carboxylic acid or acrylic monomers

suitable for use in the present invention are C_3-C_6

monoethylenically unsaturated monocarboxylic acids,

and the alkaline metal and ammonium salts thereof.

The C_3-C_6 monoethylenically unsaturated monocarboxylic

acids include acrylic acid, methacrylic acid, crotonic

acid, vinyl acedic acid, and acryloxypropionic acid.

Acrylic acid and methacrylic acid are the preferred

monoethylenically unsaturated monocarboxylic acid

monomers.

Another class of carboxylic acid monomers

suitable for use in the present invention are C_4-C_6

monoethylenically unsaturated dicarboxylic acids and

the alkaline metal and ammonium salts thereof, and the

anhydrides of the cis dicarboxylic acids. Suitable

examples include maleic acid, maleic anhydride,

itaconic acid, mesaconic acid, fumaric acid, and

citraconic acid. Maleic anhydride and itaconic acid

are preferred monoethylenically unsaturated

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dicarboxylic acid monomers.

The acid monomers useful in this invention may be in their acid forms or in the form of the alkaline metal or ammonium salts of the acid. Suitable bases useful for neutralizing the monomer acids includes sodium hydroxide, ammonium hydroxide, potassium hydroxide, and the like. The acid monomers may be neutralized to a level of from 0 to 50% and preferably from 0 to about 20%. More preferably, the carboxylic acid monomers are used in the completely neutralized form.

In addition, up to 100% by weight of the total polymerizable monomers may be monoethylenically unsaturated carboxylic acid-free monomers. Typical monoethylenically unsaturated carboxylic acid-free monomers suitable for use in the invention include alkyl esters of acrylic or methacrylic acids such as methyl acrylate, ethyl acrylate, butyl acrylate; hydroxyalkyl esters of acrylic or methacrylic acid such as hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate, and hydroxypropyl methacrylate; acrylamide, methacrylamide, N-tertiary butylacrylamide, N-methylacrylamide, N,N-dimethyl acrylamide; acrylonitrile, methacrylonitrile, dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, phosphoethyl methacrylate, N vinyl pyrrolidone, N-vinylformamide, N-vinylimidazole, vinyl

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acetate, styrene, hydroxylated styrene,
styrenesulfonic acid and salts thereof, vinylsulfonic
acid and salts thereof, and 2-acrylamido-2-
methylpropanesulfonic acid and salts thereof.

5   Other suitable comonomers include acrylamides,
alkyl and aryl amide derivatives thereof, and
quaternized alkyl and aryl acrylamide derivatives.

Monomers, polymers and copolymers of the present
invention can, in embodiments, be separated from one
10   another or from the polymerization reaction mixture
by, for example, changing the pH of the reaction media
and other well-known conventional separation
techniques.

In the (meth)acrylate polymerization of the
15   present invention, reactions can be supplemented with
a solvent or co-solvent to help insure that the
reaction mixture remains a homogeneous single phase
throughout the monomer conversion. However, in the
preferred embodiment, the (meth)acrylate
20   polymerization reactions are carried out in the
absence of a solvent.

Exemplary solvent or co-solvents useful in the
present invention include compatible aliphatic
alcohols, glycols, ethers, glycol ethers,
25   pyrrolidones, N-alkyl pyrrolidones, N-alkyl
pyrrolidones, polyethylene glycols, polypropylene
glycols, amides, carboxylic acids and salts thereof,

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esters, organosulfides, sulfoxides, sulfones, alcohol
derivatives, hydroxyether derivatives such as
CARBITOL® or CELLOSOLVE®, amino alcohols, ketones, and
the like, derivative thereof, and mixtures thereof.
5   Specific examples include ethylene glycol, propylene
glycol, diethylene glycol, glycerine, dipropylene
glycol, tetrahydrofuran, and the like, and mixtures
thereof. When mixtures of water and water soluble or
miscible organic liquids are selected as the reaction
10   media, the water to co-solvent weight ratio typically
ranges from about 100:0 to about 10:90, and preferably
from about 97:3 to about 25:75.

    Temperature of the polymerization may range from
about 80°C to about 160°C, preferably from about 110°C
15   to about 130°C. At temperatures above about 180°C,
conversion of the monomer into polymer decreases and
uncertain and undesirable by-products are formed.
Frequently, these by-products discolor the polymer
mixture and may necessitate a purification step to
20   remove them or they may be intractable.

    Since solvent and co-solvent admixtures can be
used as the reaction media, the elevated temperatures
of the polymerization require that the polymerization
reactor be equipped to operate at elevated pressure.
25   In general it is preferred to conduct the
polymerization at from about 10 to about 2000 lbs. per
square inch (psi), and more preferably at from about

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50 to about 1000 (psi).

Additives such as (a) camphorsulphonic acid
(CSA), or (b) 2-fluoro-1-methyl pyridinium p-toluene
sulfonate (FMPTS) having the chemical formulations
5   shown below, can be added to the polymerization
mixture to significantly increase the rate of
polymerization. These additives and their usefulness
in a stable free radical polymerization process are
discussed in detail in E.P. 735,052, the disclosure of
10   which is incorporated herein by reference.

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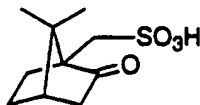
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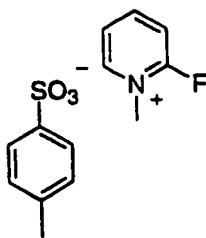
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Batch or metered addition of CSA to (meth)acrylate
polymerizations with our nitroxides further enhances
the monomer conversion. The polymers obtained from
these acid accelerated polymerizations can be chain-
25   extended with styrene to form block copolymers.

The molar ratio of nitroxide agent to free
radical initiator is from about 1:1 to 10:1. The

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molar ratio of nitroxide agent to free radical

initiator is preferably from about 1.3:1 to 1.7:1.

The influence of the ratio of initiator to stable

free radical is significant in the polymerization of

5   n-butyl acrylate when AIBN is used as the initiator.

First-order plots of polymerization conducted in the

presence of AIBN and the C7 nitroxide at 130°C show

that at a 1:1.6 ratio, the first-order plot becomes

more linear. Below this ratio, an exotherm is often

10   observed, the molecular weight does not increase with

conversion, and the polydispersity is broad. Above

this ratio molecular weight increases with increasing

conversion. The exact stoichiometry is extremely

important: 1:1.60 often gives an exotherm, whereas

15   1:1.70 gives a slow but controlled polymerization.

The slightest experimental error or the presence of

small amounts of impurities, then, can give widely

varying results.

When benzoyl peroxide (BPO) is used as the

20   initiator as opposed to AIBN, the polymerizations are

insensitive toward the ratio of initiator to stable

free radical. In general, broader polydispersities

(>2) are also observed.

The processes of the present invention provide,

25   in embodiments, a conversion rate or degree of

polymerization as high as 95% by weight.

The processes of the present invention weight

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average molecular weights ranging from about 500 to about 200,000 and more preferably from about 2000 to about 100,000 while maintaining narrow polydispersity.

Applications of (meth)acrylate block copolymers or styrene block copolymers or styrene or (meth)acrylate homopolymers can include toner compositions, adhesives, cellulosic fiber binders, compatibilizers for thermoplastic blends, emulsifiers, thickeners, processing aids for thermoplastic resins, pigment dispersants, coatings, asphalt modifiers, molded articles, sheet molding compounds, and impact modifiers.

The present invention will now be described in greater detail in the following examples.

The styrene and n-butyl acrylate used in each of the foregoing examples were obtained from Aldrich. The inhibitors were removed using t-butyl catechol and hydroquinone inhibitor remover (Aldrich). Reaction samples were diluted with either THF or CH_2Cl_2 for GC analysis, which was done on a HP5890 GC with a HP-1 column and thermal conductivity detector running at a constant 150°C oven temperature. The internal reference used was ortho-dichlorobenzene. GPC samples were evaporated by air drying and dried overnight at 60°C in a vacuum oven. Molecular weights reported in the examples were determined by GPC in THF versus polystyrene standards.

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As used in the examples, M_n refers to the number

average molecular weight, M_w refers to the weight

average molecular weight, M_p refers to peak molecular

weight, and PDI, the polydispersity ratio, is the

5   ratio of the weight average molecular weight to the

number average molecular weight.

EXAMPLE 1

N-tertbutyl-2-methyl-1,2-propanediamine (0.1

10   mol), chloroform (0.15 mol), acetone (0.2 mol),

Aliquat 336 tricaprylylmethylammonium chloride (0.003

mol), and 100 mL toluene were mixed and cooled to 10°C

under nitrogen atmosphere. Solid sodium hydroxide

beads (0.5 mol) were added in 30 minutes to keep the

15   temperature below 20°C. After the addition and three

hours stirring at 15-20°C, the reaction was filtered,

dried over sodium sulfate and concentrated to afford

greater than 90% yield of product, which was about 95%

pure by gas chromatograph. The solidified product was

20   recrystallized from hexanes to afford an analytically

pure sample.

The amine was oxidized in the conventional manner

to the corresponding dimethyl nitroxide by following

procedures known by those skilled in the art and

25   described in the reference Rozantzev, E. G., "Free

Nitroxyl Radicals" (Plenum Press 1970).

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EXAMPLE 2

Example 1 was repeated under identical
conditions, with the exception that 4-methyl-2-
pentanone was substituted for the acetone to give the

5   iBu nitroxide.

EXAMPLE 3

Example 1 was repeated under identical
conditions, with the exception that acetophenone was

10   substituted for the acetone to give the phenyl

nitroxide.

EXAMPLE 4

Example 1 was repeated under identical conditions

15   with the exception that cyclopentanone was substituted

for the acetone to give the C5 nitroxide.

EXAMPLE 5

Example 1 was repeated under identical conditions

20   with the exception that cyclohexanone was substituted

for the acetone to give the C6 nitroxide.

EXAMPLE 6

Example 1 was repeated under identical conditions

25   with the exception that cycloheptanone was substituted

for the acetone to give the C7 nitroxide.

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EXAMPLE 7

2-Amino-2-methyl-1-propanol (17.8 g, 0.2 mol),
chloroform (35.8 g, 0.3 mol), cycloheptanone (45.1 g,
0.4 mol), Aliquat 336 (3.23 g, 0.008 mol), and 120 mL
toluene were mixed under nitrogen at 10°C. Sodium
hydroxide beads (40.0 g, 0.5 mol) were added in 30
minutes to keep the temperature below 20°C. After
stirring at 15-20°C for another 2 hours and 45
minutes, the reaction was filtered and rinsed with a
small amount of toluene. The solid was extracted with
2X100 mL methanol. The combined methanol solutions
were concentrated to afford 61 g of the carboxylate
intermediate. The white solid was refluxed with 80 mL
concentrated hydrochloric acid in air for 10 hours.
It was then cooled to about 75°C and 150 mL toluene
was then added. The excess acid and water were
removed with a Dean-Stark trap. The toluene solution
was concentrated and distilled to 185-195°C at 14 mmHg
to afford 35 g 3,3-hexamethylene-5,5-dimethyl-2-
oxomorpholine as a clear yellow oil, which was used to
make the nitroxide.

The amine was oxidized in the conventional manner
referenced in Example 1 to give the C7 morpholone
nitroxide.

EXAMPLE 8

Example 7 was repeated under identical conditions

- 26 -

with the exception that the cycloheptanone was

replaced with acetone to give the diMe morpholone.

EXAMPLE 9

5   Example 7 was repeated under identical conditions

with the exception that cyclohexanone was substituted

for the cycloheptanone to give the C6 morpholone.

EXAMPLE 10

10   Styrene (15g), benzoyl peroxide (0.62 mmol,

0.150g), and the C6 nitroxide (0.8 mmol, 0.125g) of

Example 5 were charged to a 150 mL cylindrical flask

with a 4-head Teflon coated head equipped with

condenser, bubbler, magnetic stir bar and two septa

15   ports. The solution was purged thoroughly with argon

for 15 minutes and then lowered into an oil bath

preheated to 140°C. The polymerization was carried

out for 6 hours. The polymer solution was diluted in

10 mL THF and precipitated into a ten times excess of

20   methanol. The polymer was filtered and dried under

vacuum overnight. A conversion of 67% (determined

gravimetrically) and a yield of 9.9 grams of

polystyrene was obtained with M_n equal to 12, 678, M_p

equal to 20, 044, M_w equal to 18, 100 and PDI is 1.42.

25

EXAMPLE 11

Example 10 was repeated under identical

- 27 -

conditions, with the exception that the dimethyl

nitroxide of Example 1 was substituted for the C6

nitroxide. A conversion of 50% (determined

gravimetrically) and a yield of 7.5 grams of

5   polystyrene were obtained with M_n equal to 12,312, M_p

equal to 15,661, M_w equal to 14,989, and PDI equal to

1.2.

EXAMPLE 12

10   Example 11 was repeated under identical

conditions, with the exception that the phenyl

nitroxide of Example 3 was substituted for the

dimethyl nitroxide. A conversion of 54% (determined

gravimetrically) and a yield of 8.1 grams of

15   polystyrene were obtained with M_n equal to 13,306, M_p

equal to 16,624, M_w equal to 15,919, and PDI equal to

1.19.

COMPARATIVE EXAMPLE 1

20   Example 10 was repeated under identical

conditions, with the exception that TEMPO was

substituted for the C6 nitroxide. A conversion of 35%

(determined gravimetrically) and a yield of 5.2 grams

of polystyrene were obtained with M_n equal to 8,174, M_p

25   equal to 11,130, M_w equal to 10,406, and PDI equal to

1.27.

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EXAMPLE 13

7 mL of *n*-butyl acrylate, 0.12 g of the isobutyl

nitroxide of Example 2, and 0.074 g of BPO were heated

at 130°C for 24 hours. A polymer having M_n equal to

5   6800 and PDI equal to 1.32 was isolated in a 40%

yield.

EXAMPLE 14

7 mL of *n*-butyl acrylate, 74 mg of BPO and 0.130

10   g of the C7 morpholone nitroxide of Example 7 were

heated at 130°C for 28 hours. A polymer having M_n

equal to 27,000 and PDI equal to 1.71 was isolated in

a 50% yield.

COMPARATIVE EXAMPLE 2

15

Example 14 was repeated under identical

conditions with the exception that 4-oxo TEMPO was

substituted for the C7 morpholone nitroxide. A

polymer having bimodal distribution was obtained in a

20   15% yield with M_n equal to 3000, PDI equal to 2.06.

EXAMPLE 15

Tetramethyl morpholone (141.3g, 0.90 mole),

molybdenum oxide (3.0 g) and ethylbenzene (720 mL)

25   were mixed and heated to 110°C under N_2 atmosphere. t-

Butyl hydroperoxide (70% aq. solution, 249.1 g, 2.49

mole) was added dropwise in 1 hour. The addition

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funnel was replaced with a distillation column and t-
butyl alcohol-water was distilled over slowly in 15
hours. The reaction content was dried over sodium
sulfate and concentrated to a dark oil, which
5   solidified on standing. The solid was recrystallized
from hexanes to obtain beige-colored crystals (155 g).

EXAMPLE 16

The styrene prepolymer end-capped with the C6
10   nitroxide formed in Example 10 (2g), n-butyl acrylate
(5g), and DMSO (5 mL) were charged into a glass
reactor of the type described in Example I, purged
thoroughly with argon for 15 minutes, and then lowered
into an oil bath preheated to 80°C. The prepolymer
15   had a M_n equal to 12,678, M_w equal to 18,100 and a
molecular weight distribution of 1.4. The
polymerization was carried out for 6 hours. Samples
were withdrawn with time to monitor the progress of
the reaction. The polymer solution was diluted with
20   THF and precipitated into a ten times excess of
methanol. The polymer was filtered and dried under
vacuum overnight.

The molecular weight data for the final polymer
obtained after precipitation into methanol was M_n equal
25   to 18,524, M_w equal to 51,899, with a molecular weight
distribution of 1.4. An increased ΔM_w of 33,799 was
obtained on formation of the block copolymer.

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Analysis of GC and NMR results indicated between 70-72% conversion of *n*-butyl acrylate. The molar incorporation of *n*-butyl acrylate in the diblock copolymer was found to be approximately 46%.

EXAMPLE 17

Example 16 was repeated under identical conditions, with the exception that after the low temperature initiation of 80°C was used for 1 hour, the polymerization temperature was increased to 100°C. The polymerization temperature in the flask, however, did not increase beyond 90°C. A yield of 6 grams of diblock copolymer was obtained corresponding to approximately 90% conversion of *n*-butyl acrylate. The molecular weight data for the diblock copolymer was M_n equal to 35,353, M_w equal to 90,288, with a molecular weight distribution of 2.55. An increase in ΔM_w of 72,188 was obtained on formation of the block copolymer. NMR analysis indicated approximately 63% molar incorporation of *n*-butyl acrylate, corresponding to approximately 100% conversion of *n*-butyl acrylate.

EXAMPLE 18

Example 16 was repeated under identical conditions with the exception that after the low polymerization temperature of 80°C was used for 1 hour, the polymerization temperature was increased to

-31-

150°C. The actual reaction temperature was between
135-140°C for 6 hours. A yield of 4.3 grams was
obtained, corresponding to approximately 61%
conversion of n-butyl acrylate. The molecular weight

5   data for the diblock copolymer was M_n equal to 16,525,
M_w equal to 40,251, and PDI equal to 2.4. NMR
indicated approximately 53% molar incorporation of n-
butyl acrylate into the block copolymer. An increase
in M_w of 22,151 was obtained for the polymer after

10   chain extension with n-butyl acrylate.

                        EXAMPLE 19

       Example 10 was repeated under identical
conditions with the exception that the C6 nitroxide

15   was replaced with the C7 nitroxide of Example 6. The
reaction was stopped at 52% conversion, the resultant
prepolymer having M_n equal to 10,735, M_w equal to
13,221, and PDI equal to 1.23

       The prepolymer (2g) and n-butyl acrylate (10 mL)

20   were charged into a glass reactor of the type
described in Example 10, purged thoroughly with argon
for 15 minutes, and then lowered into an oil bath
preheated to 140°C. The prepolymer had an M_n equal to
10,735, M_w equal to 13,221, and a molecular weight

25   distribution of 1.23. The temperature inside the
flask was at 130°C. The polymerization was carried
out for approximately 23 hours. The polymer solution

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was diluted with THF and precipitated into a ten times

excess of methanol. The polymer was filtered and

dried under vacuum overnight.

The molecular weight data for the final polymer

obtained after precipitation into methanol was M_n equal

to 20,720 and M_w equal to 27,881, with a PDI equal to

1.34. Samples withdrawn from the reaction mixture

indicated that the conversion increased with time.

EXAMPLE 20

Example 19 was repeated under identical

conditions. Samples were withdrawn over time and are

characterized in **TABLE II**.

TABLE II

	SAMPLE 1	SAMPLE 2	SAMPLE 3
M_n	17,534	19,555	21,881
M_w	21,192	24,534	28,006
PDI	1.29	1.255	1.28
Percentage Conversion	29%	48%	50%

EXAMPLE 21

Example 10 was repeated under identical

conditions with the exception that 45 mL styrene, 0.19

g of the dimethyl morpholone nitroxide of Example 8

and 0.206 g BPO were used. The reaction was stopped

- 33 -

at 47% conversion, the resultant prepolymer having M_n =
18,500 M_w equal to 26,800 and PDI equal to 1.45.

The styrene prepolymer end capped with the DiMe
morpholone nitroxide (M_n = 18,500, M_w = 26,800, PDI =
5   1.45) (5g) and n-butyl acrylate (10 mL) were charged
into a glass reactor of the type described in Example
10, purged thoroughly with argon for 15 minutes and
then lowered into an oil bath preheated to 140°C. The
polymerization was carried out for approximately 22
10   hours. The polymer solution was diluted with THF and
precipitated into a ten times excess of methanol. The
polymer was filtered and dried under vacuum overnight.
The molecular weight data for the final polymer
obtained after precipitation into methanol is set out
15   in **TABLE III**.

<u>EXAMPLE 22</u>

Example 10 was repeated under identical
conditions with the exception that 30 mL styrene, 0.36
20   g of the C7 morpholone nitroxide of Example 7 and 0.3
g of BPO were used. The reaction was stopped at 70%
conversion, the resultant prepolymer having M_n equal to
14,800, M_w = 18,300, and PDI = 1.24.

Example 21 was then repeated under identical
25   conditions, except that the styrene prepolymer end
capped with the C7 morpholone nitroxide (M_n = 14,800,
M_w = 18,300, PDI = 1.24) was substituted for the

- 34 -

prepolymer of Example 21 and an additional 10 mL of *n*-butyl acrylate was used. The molecular weight data for the final polymer obtained after precipitation into methanol is set out in **TABLE III**, below. Fig. 1,

5   a plot of molecular weight of the styrene-*n*-butyl acrylate block copolymer versus percent conversion, shows that molecular weight evolution with regard to conversion occurred in a linear fashion indicating a controlled free radical polymerization and a clean

10   formation of the block copolymer. Molecular weights were determined by GPC in THF versus polystyrene standards. Data points were taken at 0, 3, 6, 9 and 23 hours.

15

M_n

25000

20000

15000

10000

5000

0   10   20

20
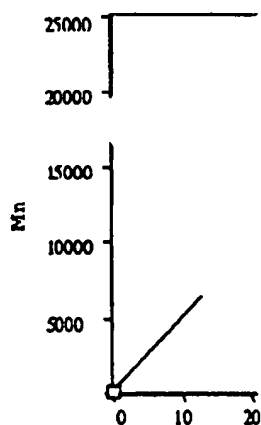
EXAMPLE 23

Example 10 was repeated under identical

25   conditions with the exception that the C6 nitroxide was replaced with the diMe morpholone nitroxide of Example 8. The reaction was stopped at 80%

-35-

conversion, the resultant prepolymer having M_n equal to

12,900, M_w = 19,100, and PDI equal to 1.24.

Example 22 was then repeated under identical

conditions, except that the styrene prepolymer end

5   capped with the diMe morpholone nitroxide (M_n = 14,800,

M_w = 18,000, PDI = 1.47) was substituted for the

prepolymer of Example 10 and an additional 10 mL of *n*-

butyl acrylate was used. The molecular weight data

for the final polymer obtained after precipitation

10   into methanol is set out in **TABLE III**, below.

TABLE III

Example No.	Polystyrene-nitroxide (g, Mn,)	n-butylacrylate (mL)	M_n(diblock) Exptal	M_n(diblock) Targeted	Conversion	PDI
23	C-dimethyl (10g, 12K)	20	22,400	36,000	65	1.54
21	C-dimethyl 5g, 18K)	10	36,900	51,600	80	1.7
22	C-7 10g, 15K)	20	34,500	41,000	85	1.68

20   **EXAMPLE 24**

5 mL styrene, 116 mg BPO, and 174 mg of the

dicyclohexyl nitroxide were heated at 130°C for 4

hours. A polymer was obtained in 66% yield with M_n =

6200, PDI = 1.40. The synthesis procedure used for

25   the dicyclohexyl nitroxide is known and is described

with particularity in Yoshioka, T., Mori, E., and

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Murayama, K., "Synthesis and ESR Spectral properties
of Hindered Piperazine N-Oxyls", Bulletin of the
Chemical Society of Japan, Vol. 45, pp. 1855-1860
(1972).

5   The styrene prepolymer end-capped with the
dicyclohexyl nitroxide $(M_n = 6200$, PDI = 1.40) (0.5 g)
was dissolved in 3 mL of n-butyl acrylate and heated
at 130°C for 20 hours. A block copolymer having M_n
equal to 8400 and PDI equal to 1.34 was obtained after

10   10% of the monomer was converted.

EXAMPLE 25

       A three neck, 25 mL roundbottom flask equipped
with a mechanical stirrer, temperature probe, argon

15   inlet and condenser was charged with 5 mL styrene, 1
mL ortho-dichlorobenzene and 0.36 g of the n-butyl
acrylate prepolymer obtained in Example 8 having an
isobutyl nitroxide endgroup $(M_n = 6800$, PDI = 1.32).
Argon was bubbled through the solution while stirring

20   for 1 hour and the reaction mixture was lowered into a
preheated oil bath at 130°C. The reaction was carried
out overnight and was too viscous to sample for GC
conversion. GPC analysis in THF showed a molecular
weight increase to a M_n equal to 53,000, and PDI equal

25   to 2.2. GPC analysis in trichlorobenzene showed only
a very small amount of n-butyl acrylate prepolymer
remaining, indicating that the prepolymer contained

-37-

virtually no dead chains.

EXAMPLE 26

A 100 mL reaction flask with a 45/50 joint was equipped with a reactor head and a stirbar. Through the center joint of the reactor head a near-infrared probe was fitted with teflon tape (UPO instruments, model Insight IV fiber optic spectrometer). The other joints were used for a condenser with bubbler, Argon inlet, temperature probe and sample port. The flask was charged with 54 g n-butyl acrylate, 0.95 g of the C7 morpholone nitroxide of Example 7, 0.34 g AIBN and 7.5 mL ortho-dichlorobenzene as the internal standard. A 25 mL syringe was filled with a 0.233 M solution of triflic acid in diethyl carbonate and fitted on a syringe pump. Through the sample port of the reactor, a syringe filled with 0.20 M_n C7 morpholone nitroxide in diethyl carbonate was fitted. The mixture was heated at 130°C and the reaction conversion was followed by GC and near infrared. Acid was metered in slowly until a rise in the reaction temperature, or increase in conversion was noted. At this point 0.1 mL of the nitroxide solution was injected which slowed the polymerization instantaneously. Addition of acid and nitroxide was continued while keeping the temperature of the reactor below 135°C. At the end of the polymerization, a polymer was obtained in 91%

- 38 -

yield with M_n equal to 6300, PDI equal to 4.3. This polymer was purified by precipitation from methanol to remove any impurities.

<u>**EXAMPLE 27**</u>

Example 26 was repeated under identical conditions with the exception that 198 mg of the isobutyl nitroxide of Example 2 was substituted for the C7 morpholone nitroxide. A polymer having M_n equal to 81,900 and PDI equal to 2.07 was obtained in 82% yield.

<u>**EXAMPLE 28**</u>

The prepolymer of Example 27 (1 g) was heated in 5 mL of styrene with 0.5 mL of ortho-dichlorobenzene as an internal standard. After 16 hours at 130°C a polymer having M_n equal to 164,000 and PDI equal to 2.50 was isolated. GPC analysis in trichlorobenzene showed no trace of the starting prepolymer indicating that the acrylate-styrene block copolymer had formed completely.

<u>**EXAMPLE 29**</u>

5 mL of *n*-butyl acrylate and 48 mg of the adduct of ethylbenzene and dimethyl morpholone nitroxide formed in Example 15 were heated at 130°C for 40 hours. A polymer having M_n equal to 13,900 and PDI

-39-

equal to 1.8 was obtained in 77% yield.

EXAMPLE 30

Styrene (2.5 g), AIBN (0.11 g) and the C7
morpholone of Example 7 (0.24 g) were heated at 130°C
for 4 hours. The prepolymer obtained in a 40% yield
by precipitating the reaction in methanol had M_n equal
to 940 and a PDI equal to 1.12.

The prepolymer (1 g) was then heated in t-butyl
acrylate at 130°C for 6 hours. The conversion by GC
of t-butyl acrylated was 44%. The resultant block
copolymer had M_n equal to 1600 and a PDI equal to 1.46.

COMPARATIVE EXAMPLE 3

A polystyrene prepolymer with a TEMPO endgroup
(2g) having M_n equal to 20,500 and PDI equal to 1.28
was heated with 5 mL of t-butyl acrylate and 2 mL of
DMSO at 128°C. After 5 hours, the polymer obtained
contained no acrylate as determined by NMR.

EXAMPLE 31

The prepolymer of Example 22 (0.5 g) was heated
in 2 mL dimethyl aminoethyl acrylate at 130°C for 24
hours. The conversion of the acrylate monomer by GC
was determined to be 37%. The polymer obtained was
completely soluble in methanol and the molecular

- 40 -

weight was determined by NMR to be 29,500, showing

that a clean block copolymer was obtained.

EXAMPLE 32

5   The block copolymer of Example 22 (7 g) was

heated in styrene at 140°C for 17 hours. A triblock

copolymer (18 g) was obtained having M_n equal to 72,600

and PDI equal to 2.7.

10   The stable free radical mediated polymerization

process claimed in a number of patents results in

narrow polydispersity resins and linear molecular

weight growth with conversion. This opens the

possibility to synthesize block copolymers. The SFRP

15   process depends uniquely on the stable free radical

mediator used. The patents cited above use TEMPO and

TEMPO derivatives and show examples of polymerization

of styrene and styrene derivatives. However, as shown

in the comparative Examples, these nitroxides do not

20   enable efficient polymerization of acrylates either as

homopolymers or in combination with other monomers to

form block copolymers.

      We have found, unexpectedly, that by altering the

nitroxide structure to a highly hindered piperazone or

25   morpholone nitroxide, acrylate polymerization mediated

by these stable free radicals is feasible with high

efficiency. Specifically, we have shown improved

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homopolymerization of acrylates using these

nitroxides. We have also shown that block copolymers

can be formed in very high yields starting with either

styrene prepolymers endcapped with the new nitroxides

5   or acrylate prepolymers endcapped with the new

nitroxides. Indeed, the block copolymer formation

occurs in a controlled fashion with formation of

narrow polydispersity resins. These significant

improvements are due to the structural differences

10   between piperazone and morpholone nitroxides, on the

one hand, and TEMPO and its derivatives, on the other.
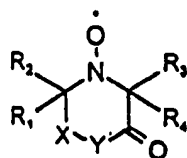
The invention has been described with reference

to preferred and alternate embodiments. Obviously,

modifications and alterations will occur to others

15   upon the reading and understanding of this

specification. It is intended to include all such

modifications and alterations insofar as they come

within the scope of the appended claims or the

equivalents thereof.

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Having thus described the invention, it is

claimed:

1.   A free radical polymerization process for

the preparation of a thermoplastic resin or resins

comprising the step of:

heating from about 80° to about 160°C a

mixture of a free radical initiator, at least one

polymerizable monomer compound, and a stable free

radical agent comprising a nitroxyl radical having the

following formula:

wherein X is CH_2 or C=O, Y is O or N-R, R, R_1, R_2, R_3,

and R_4 are independently selected from the group

consisting of aryl, alkyl having from 1 to about 24

carbon atoms, cycloalkyl having from 5 to about 7

carbon atoms, aralkyl having from 7 to about 20 carbon

atoms, cyanoalkyl having from 2 to about 12 carbon

atoms, ether having from 4 to about 18 carbon atoms,

and hydroxyalkyl having from 1 to about 18 carbon

atoms; and

R_1 and R_2 together, or R_3 and R_4 together, or

each pair, may be cyclized forming a ring having from

about 5 to about 14 carbon atoms to form said

- 43 -

thermoplastic resin or resins with a polydispersity of about 1.0 to about 3.0.

2.   The process of claim 1 wherein said polymerizable monomer compound is a monoethylenically unsaturated carboxylic acid-free monomer selected from the group consisting of alkyl esters of (meth)acrylic acid, hydroxyalkyl esters of (meth)acrylic acid, (meth)acrylamide, (meth)acrylonitrile, vinyl acetate, and vinyl and vinylidene halides.

3.   The process of claim 2 wherein said alkyl esters of (meth)acrylic acid are selected from the group consisting of methyl acrylate, ethyl acrylate, and butyl acrylate.

4.   The process of claim 2 wherein said hydroxyalkyl esters of (meth)acrylic acid are selected from the group consisting of hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate and hydroxypropyl methacrylate.

5.   The process of claim 1 wherein said polymerizable monomer compound is alkyl acrylate or alkyl methacrylate.

6.   The process of claim 1 wherein said

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polymerizable monomer compound is styrene or styrene
derivatives.

7.   The process of claim 1 wherein said
polymerizable monomer compound is *n*-butyl acrylate or
acrylate derivatives.

8.   The process of claim 1 wherein said
polymerizable monomer compound is *t*-butyl acrylate or
acrylate derivatives.

9.   The process of claim 1 wherein said stable
free radical agent is selected from the group
consisting of 1-tertbutyl-3,3,5,5-tetramethyl-2-
piperazinone-oxide, 3-isobutyl-1-isopropyl-3,5,5-
5   trimethyl-2-piperazinone-oxide, 1-isopropyl-3-phenyl-
3,5,5-trimethyl-2-piperazinone-oxide, 3,3-
tetramethylene-5,5-dimethyl-1-isopropyl-2-
piperazinone-oxide, 3,3-pentamethylene-5,5-dimethyl-1-
isopropyl-2-piperazinone-oxide, 3,3-hexamethylene-5,5-
10   dimethyl-1-isopropyl-2-piperazinone-oxide, and bis-
3,3,5,5-pentamethylene-2,6-piperazinone-dione-oxide.

10.   The process of claim 1 wherein said stable
free radical agent is selected from the group
consisting of 3,3,5,5-tetramethyl-2-morpholone-oxide,
3,3-pentamethylene-5,5-dimethyl-2-morpholone-oxide,

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and 3,3-hexamethylene-5,5-dimethyl-2-morpholone oxide.

11.   The process of claim 1 wherein said free
radical agent is 3,3-hexamethylene-5,5-dimethyl-2-
morpholone oxide.

12.   The process of claim 1 wherein the molar
ratio of said stable free radical agent to said free
radical initiator is from about 1:1 to about 10:1.

13.   The process of claim 12 wherein the molar
ratio of said stable free radical agent to said free
radical initiator is from about 1.3:1 to about 1.7:1.

14.   The process of claim 1 wherein the heating
of said mixture is conducted in a solvent or diluent.

15.   The process of claim 14 wherein said solvent
is selected from the group consisting of ethylene
glycol, propylene glycol, diethylene glycol,
glycerine, dipropylene glycol, tetrahydrofuran and
mixtures thereof.

16.   The process of claim 1 wherein said free
radical initiator is selected from the group
consisting of peroxo compounds containing at least one
O—O group.

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17. The process of claim 1 wherein said free
radical initiator is selected from the group
consisting of hydrogen peroxide, t-butyl
hydroperoxide, t-butyl perbenzoate, t-amyl
5   perbenzoate, t-butyl peroctoate, t-amyl peroctoate,
ditertiary butyl peroxide, tertiary-amyl
hydroperoxide, dibenzoyl peroxide, potassium
persulfate, and methyl ethyl ketone peroxide.

18. The process of claim 1 further comprising
adding an inorganic acid, organic sulfonic acid or
organic carboxylic acid during heating of said mixture
thereby increasing the rate of formation of said
5   thermoplastic resin or resins from said polymerization
of said monomer compound.

19. The process of claim 18 wherein said organic
sulfonic acid is camphorsulphonic acid.

20. The process of claim 19 wherein the step of
adding said camphorsulphonic acid is conducted as
batch or metered.

21. The process of claim 1 wherein the heating
of said mixture is conducted with said mixture as a
suspension in water or in a polar liquid.

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22. The process of claim 1 wherein the heating
of said mixture is conducted from about 110°C to about
130°C.

23. The process of claim 1 wherein said
polymerizable monomer compound is selected from the
group consisting of styrene and derivatives thereof,
conjugated dienes and derivatives thereof, acrylates
5   and derivatives thereof, and mixtures thereof.

24. The process of claim 1 wherein said monomer
to polymer conversion is up to 95 percent by weight.

25. The process of claim 1 further comprising
the steps of:
        isolating said thermoplastic resin or
resins;
5   followed by washing and drying said
thermoplastic resin or resins.

26. The process of claim 1 wherein the weight
average molecular weight of the thermoplastic resin or
resins is from about 2,000 to about 100,000.

27. A free radical polymerization process for
the preparation of a thermoplastic resin or resins

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comprising the step of:

heating from about 80°C to about 160°C a

5   mixture of at least one polymerizable monomer compound

and a preformed nitroxide adduct having the following

formula:

$$\begin{array}{c} O-R_5 \\ | \\ R_2\quad N\quad R_3 \\ \diagdown\diagup\quad|\quad\diagdown\diagup \\ R_1\quad X-Y\quad R_4 \\ O \end{array}$$

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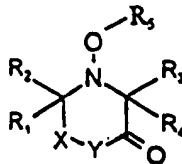
wherein X is CH_2 or $C=O$, Y is O or $N-R$, R, R_1, R_2, R_3,

R_4, and R_5 are independently selected from the group

consisting of aryl, alkyl having from 1 to about 24

carbon atoms, cycloalkyl having from 5 to about 7

15   carbon atoms, aralkyl having from 7 to about 20 carbon

atoms, cyanoalkyl having from 2 to about 12 carbon

atoms, ether having from 4 to about 18 carbon atoms,

and hydroxyalkyl having from 1 to about 18 carbon

atoms; and

20   R_1 and R_2 together, or R_3 and R_4 together, or

each pair, may be cyclized forming a ring having from

about 5 to about 14 carbon atoms to form said

thermoplastic resin or resins with a polydispersity

from about 1.0 to about 3.0.

28.   The process of claim 27 wherein said

polymerizable monomer compound is a monoethylenically

unsaturated carboxylic acid-free monomer selected from

the group consisting of alkyl esters of (meth)acrylic

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acid, hydroxyalkyl esters of (meth)acrylic acid,
(meth)acrylamide, (meth)acrylonitrile, vinyl acetate,
and vinyl and vinylidene halides.

29.   The process of claim 28 wherein said alkyl
esters of (meth)acrylic acid are selected from the
group consisting of methyl acrylate, ethyl acrylate,
and butyl acrylate.

30.   The process of claim 28 wherein said
hydroxyalkyl esters of (meth)acrylic acid are selected
from the group consisting of hydroxyethyl acrylate,
hydroxypropyl acrylate, hydroxyethyl methacrylate and
5   hydroxypropyl methacrylate.

31.   The process of claim 27 wherein said
polymerizable monomer compound is alkyl acrylate or
alkyl methacrylate.

32.   The process of claim 27 wherein said
polymerizable monomer compound is styrene or styrene
derivatives.

33.   The process of claim 27 wherein said
polymerizable monomer compound is n-butyl acrylate or
acrylate derivatives.

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34. The process of claim 27 wherein said polymerizable monomer compound is *t*-butyl acrylate or acrylate derivatives.

35. The process of claim 27 further comprising adding an inorganic acid, organic sulfonic acid or organic carboxylic acid during heating of said mixture thereby increasing the rate of formation of said

5   thermoplastic resin or resins from said polymerization of said monomer compound.

36. The process of claim 35 wherein said organic sulfonic acid is camphorsulphonic acid.

37. The process of claim 36 wherein the step of adding said camphorsulphonic acid is conducted as a batch or metered process.

38. The process of claim 27 wherein the heating of said mixture is conducted from about 110°C to about 130°C.
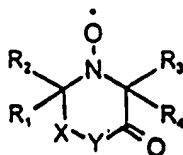
39. The process of claim 27 wherein said polymerizable monomer compound is selected from the group consisting of styrene and derivatives thereof, conjugated dienes and derivatives thereof, acrylates

5   and derivatives thereof, and mixtures thereof.

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40. The process of claim 27 wherein said monomer
to polymer conversion is up to 95 percent by weight.

41. A free radical polymerization process for
the preparation of a (meth)acrylate containing block
copolymer comprising the steps of:

(a) heating from about 80° to about 160°C a
5   first mixture of a free radical initiator, a first
polymerizable monomer compound, and a stable free
radical agent comprising a nitroxyl radical having the
following formula:

10

wherein X is CH_2 or C=O, Y is O or N-R, R, R_1, R_2, R_3,
and R_4 are independently selected from the group
15   consisting of aryl, alkyl having from 1 to about 24
carbon atoms, cycloalkyl having from 5 to about 7
carbon atoms, aralkyl having from 7 to about 20 carbon
atoms, cyanoalkyl having from 2 to about 12 carbon
atoms, ether having from 4 to about 18 carbon atoms,
20   and hydroxyalkyl having from 1 to about 18 carbon
atoms; and

R_1 and R_2 together, or R_3 and R_4 together, or
each pair, may be cyclized forming a ring having from

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about 5 to about 14 carbon atoms to form a prepolymer;

25   and

(b) heating from about 80°C to about 160°C a
second mixture of said prepolymer and a second
polymerizable monomer compound, said second
polymerizable monomer compound being different than

30   said first polymerizable compound.

42.   The process of claim 41 wherein said first
or second polymerizable monomer compound is a
monoethylenically unsaturated carboxylic acid-free
monomer selected from the group consisting of alkyl

5   esters of (meth)acrylic acid, hydroxyalkyl esters of
(meth)acrylic acid, (meth)acrylamide,
(meth)acrylonitrile, vinyl acetate, and vinyl and
vinylidene halides.

43.   The process of claim 42 wherein said alkyl
esters of (meth)acrylic acid are selected from the
group consisting of methyl acrylate, ethyl acrylate,
and butyl acrylate.

44.   The process of claim 42 wherein said
hydroxyalkyl esters of (meth)acrylic acid are selected
from the group consisting of hydroxyethyl acrylate,
hydroxypropyl acrylate, hydroxyethyl methacrylate and

5   hydroxypropyl methacrylate.

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45. The process of claim 41 wherein said first or second polymerizable monomer compound is alkyl acrylate or alkyl methacrylate.

46. The process of claim 41 wherein said first or second polymerizable monomer compound is styrene or styrene derivatives.

47. The process of claim 41 wherein said first or second polymerizable monomer compound is *n*-butyl acrylate or acrylate derivatives.

48. The process of claim 41 wherein said first or second polymerizable monomer compound is *t*-butyl acrylate or acrylate derivatives.

49. The process of claim 41 wherein said stable free radical agent is selected from the group consisting of 1-tertbutyl-3,3,5,5-tetramethyl-2-piperazinone-oxide, 3-isobutyl-1-isopropyl-3,5,5-
5   trimethyl-2-piperazinone-oxide, 1-isopropyl-3-phenyl-
3,5,5-trimethyl-2-piperazinone-oxide, 3,3-
tetramethylene-5,5-dimethyl-1-isopropyl-2-
piperazinone-oxide, 3,3-pentamethylene-5,5-dimethyl-1-
isopropyl-2-piperazinone-oxide, 3,3-hexamethylene-5,5-
10   dimethyl-1-isopropyl-2-piperazinone-oxide, and bis-

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3,3,5,5-pentamethylene-2,6-piperazinone-dione-oxide.

50. The process of claim 41 wherein said stable
free radical agent is selected from the group
consisting of 3,3,5,5-tetramethyl-2-morpholone-oxide,
3,3-pentamethylene-5,5-dimethyl-2-morpholone-oxide,
and 3,3-hexamethylene-5,5-dimethyl-2-morpholone oxide.

51. The process of claim 41 wherein said free
radical agent is 3,3-hexamethylene-5,5-dimethyl-2-
morpholone oxide.

52. The process of claim 41 wherein the molar
ratio of said stable free radical agent to said free
radical initiator is from about 1:1 to about 10:1.

53. The process of claim 52 wherein the molar
ratio of said stable free radical agent to said free
radical initiator is from about 1.3:1 to about 1.7:1.

54. The process of claim 41 wherein said free
radical initiator is selected from the group
consisting of peroxo compounds containing at least one
O—O group.

55. The process of claim 41 wherein said free
radical initiator is selected from the group

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consisting of hydrogen peroxide, *t*-butyl

hydroperoxide, *t*-butyl perbenzoate, *t*-amyl

perbenzoate, *t*-butyl peroctoate, *t*-amyl peroctoate,

ditertiary butyl peroxide, tertiary-amyl

5   hydroperoxide, dibenzoyl peroxide, potassium

persulfate, and methyl ethyl ketone peroxide.

56.   The process of claim 41 further comprising

adding an inorganic acid, organic sulfonic acid or

organic carboxylic acid during heating of said mixture

thereby increasing the rate of formation of said

5   thermoplastic resin or resins.

57.   The process of claim 56 wherein said organic

sulfonic acid is camphorsulphonic acid.

58.   The process of claim 57 wherein the step of

adding said camphorsulphonic acid is conducted as

batch or metered.

59.   The process of claim 41 wherein the heating

of said first or second mixture is conducted from
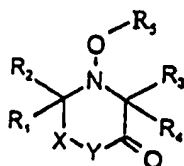
about 110˚C to about 130˚C.

60.   The process of claim 41 wherein said

polymerizable monomer compound is selected from the

group consisting of styrene and derivatives thereof,

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conjugated dienes and derivatives thereof, acrylates
and derivatives thereof, and mixtures thereof.

61.   A free radical polymerization process for
the preparation of a (meth)acrylate containing block
copolymer comprising the steps of:

(a)   heating from about 80°C to about 160°C
a first mixture of a first polymerizable monomer
compound and a preformed nitroxide adduct having the
following formula:

$$\begin{array}{c} R_2 \\ R_1 \end{array} \overset{\displaystyle O-R_5}{\underset{X-Y}{\overset{|}{\underset{\|}{N}}}} \begin{array}{c} R_3 \\ R_4 \\ O \end{array}$$

wherein X is CH_2 or C=O, Y is O or N—R, R, R_1, R_2, R_3,
R_4, and R_5 are independently selected from the group
consisting of aryl, alkyl having from 1 to about 24
carbon atoms, cycloalkyl having from 5 to about 7
carbon atoms, aralkyl having from 7 to about 20 carbon
atoms, cyanoalkyl having from 2 to about 12 carbon
atoms, ether having from 4 to about 18 carbon atoms,
and hydroxyalkyl having from 1 to about 18 carbon
atoms; and

R_1 and R_2 together, or R_3 and R_4 together, or
each pair, may be cyclized forming a ring having from
about 5 to about 14 carbon atoms to form a prepolymer;
and

(b)   heating from about 80°C to about 160°C a

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25   second mixture of said prepolymer and a second

polymerizable monomer compound, said second

polymerizable monomer compound being different than

said first polymerizable compound.

62.   The process of claim 61 wherein said first

or second polymerizable monomer compound is a

monoethylenically unsaturated carboxylic acid-free

monomer selected from the group consisting of alkyl

5   esters of (meth)acrylic acid, hydroxyalkyl esters of

(meth)acrylic acid, (meth)acrylamide,

(meth)acrylonitrile, vinyl acetate, and vinyl and

vinylidene halides.

63.   The process of claim 62 wherein said alkyl

esters of (meth)acrylic acid are selected from the

group consisting of methyl acrylate, ethyl acrylate,

and butyl acrylate.

64.   The process of claim 62 wherein said

hydroxyalkyl esters of (meth)acrylic acid are selected

from the group consisting of hydroxyethyl acrylate,

hydroxypropyl acrylate, hydroxyethyl methacrylate and

5   hydroxypropyl methacrylate.

65.   The process of claim 61 wherein said first

or second polymerizable monomer compound is alkyl

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acrylate or alkyl methacrylate.

66.   The process of claim 61 wherein said first or second polymerizable monomer compound is styrene or styrene derivatives.

67.   The process of claim 61 wherein said first or second polymerizable monomer compound is n-butyl acrylate or acrylate derivatives.

68.   The process of claim 61 wherein said first or second polymerizable monomer compound is t-butyl acrylate or acrylate derivatives.

69.   The process of claim 61 further comprising adding an inorganic acid, organic sulfonic acid or organic carboxylic acid during heating of said mixture thereby increasing the rate of formation of said

5   thermoplastic resin or resins.

70.   The process of claim 69 wherein said organic sulfonic acid is camphorsulphonic acid.

71.   The process of claim 70 wherein the step of adding said camphorsulphonic acid is conducted as batch or metered.
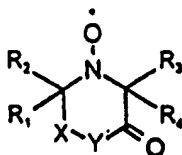
72.   The process of claim 61 wherein the heating
of said first or second mixture is conducted from
about 110°C to about 130°C.

73.   The process of claim 61 wherein said first
or second polymerizable monomer compound is selected
from the group consisting of styrene and derivatives
thereof, conjugated dienes and derivatives thereof,

5   acrylates and derivatives thereof, and mixtures
thereof.

74.   The process of claim 61 wherein said monomer
to polymer conversion is up to 95 percent by weight.

75.   A free radical polymerization process for
the preparation of a (meth)acrylate containing
triblock copolymer comprising the steps of:

       (a) heating from about 80° to about 160°C a

5   first mixture of a free radical initiator, a first
polymerizable monomer compound, and a stable free
radical agent comprising a nitroxyl radical having the
following formula:

10

$$
\begin{array}{c}
\overset{\displaystyle \cdot}{O} \\
R_1 \diagdown \quad | \diagup R_3 \\
\quad N \\
R_1' \diagup \quad \diagdown R_4 \\
X \diagdown Y \diagup \overset{}{C} = O
\end{array}
$$

wherein X is CH_2 or C=O, Y is O or N—R, R, R_1, R_2, R_3,

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and R_4 are independently selected from the group

consisting of aryl, alkyl having from 1 to about 24

15   carbon atoms, cycloalkyl having from 5 to about 7

carbon atoms, aralkyl having from 7 to about 20 carbon

atoms, cyanoalkyl having from 2 to about 12 carbon

atoms, ether having from 4 to about 18 carbon atoms,

and hydroxyalkyl having from 1 to about 18 carbon

20   atoms; and

R_1 and R_2 together, or R_3 and R_4 together, or

each pair, may be cyclized forming a ring having from

about 5 to about 14 carbon atoms, to form a

prepolymer;

25   (b) heating from about 80°C to about 160°C a

second mixture of said prepolymer and a second

polymerizable monomer compound, said second

polymerizable monomer compound being different than

said first polymerizable compound, to form a block

30   copolymer; and

(c) heating from about 80°C to about 160°C a

third mixture of said block copolymer and a third

polymerizable compound.

76.   The process of claim 75 wherein said first,

second, or third polymerizable monomer compound is a

monoethylenically unsaturated carboxylic acid-free

monomer selected from the group consisting of alkyl

5   esters of (meth)acrylic acid, hydroxyalkyl esters of

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(meth)acrylic acid, (meth)acrylamide,
(meth)acrylonitrile, vinyl acetate, and vinyl and
vinylidene halides.

77.   The process of claim 76 wherein said alkyl
esters of (meth)acrylic acid are selected from the
group consisting of methyl acrylate, ethyl acrylate,
and butyl acrylate.

78.   The process of claim 76 wherein said
hydroxyalkyl esters of (meth)acrylic acid are selected
from the group consisting of hydroxyethyl acrylate,
hydroxypropyl acrylate, hydroxyethyl methacrylate and
5   hydroxypropyl methacrylate.

79.   The process of claim 75 wherein said first,
second, or third polymerizable monomer compound is
alkyl acrylate or alkyl methacrylate.

80.   The process of claim 75 wherein said first,
second, or third polymerizable monomer compound is
styrene or styrene derivatives.

81.   The process of claim 75 wherein said first,
second, or third polymerizable monomer compound is n-
butyl acrylate or acrylate derivatives.

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82. The process of claim 75 wherein said first, second, or third polymerizable monomer compound is *t*-butyl acrylate or acrylate derivatives.

83. The process of claim 75 wherein said stable free radical agent is selected from the group consisting of 1-tertbutyl-3,3,5,5-tetramethyl-2-piperazinone-oxide, 3-isobutyl-1-isopropyl-3,5,5-
5   trimethyl-2-piperazinone-oxide, 1-isopropyl-3-phenyl-3,5,5-trimethyl-2-piperazinone-oxide, 3,3-tetramethylene-5,5-dimethyl-1-isopropyl-2-piperazinone-oxide, 3,3-pentamethylene-5,5-dimethyl-1-isopropyl-2-piperazinone-oxide, 3,3-hexamethylene-5,5-
10 dimethyl-1-isopropyl-2-piperazinone-oxide, and bis-3,3,5,5-pentamethylene-2,6-piperazinone-dione-oxide.

84. The process of claim 75 wherein said stable free radical agent is selected from the group consisting of 3,3,5,5-tetramethyl-2-morpholone-oxide, 3,3-pentamethylene-5,5-dimethyl-2-morpholone-oxide,
5   and 3,3-hexamethylene-5,5-dimethyl-2-morpholone oxide.

85. The process of claim 75 wherein said free radical agent is 3,3-hexamethylene-5,5-dimethyl-2-morpholone oxide.

86. The process of claim 75 wherein the molar

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ratio of said stable free radical agent to said free

radical initiator is from about 1:1 to about 10:1.

87. The process of claim 86 wherein the molar

ratio of said stable free radical agent and said free

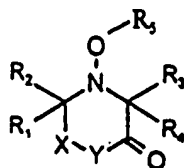radical initiator is from about 1.3:1 to about 1.7:1.

88. The process of claim 75 wherein said first,

second, or third polymerizable monomer compound is

selected from the group consisting of styrene and

derivatives thereof, conjugated dienes and derivatives

5   thereof, acrylates and derivatives thereof, and

mixtures thereof.

89. In a free radical polymerization process for

the preparation of a thermoplastic resin or resins of

the type comprising heating from about 80°C to about

160°C a mixture of a free radical initiator, a

5   nitroxide stable free radical agent, and at least one

polymerizable monomer compound, to form said

thermoplastic resin or resins having a high monomer to

polymer conversion and a narrow polydispersity,

wherein the improvement comprises:

10   said nitroxide stable free radical agent

being a nitroxide radical having the following

formula:

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wherein X is CH$_2$ or C=O, Y is O or N-R, R, R$_1$, R$_2$, R$_3$,

R$_4$, and R$_5$ are independently selected from the group

consisting of aryl, alkyl having from 1 to about 24

carbon atoms, cycloalkyl having from 5 to about 7

carbon atoms, aralkyl having from 7 to about 20 carbon

atoms, cyanoalkyl having from 2 to about 12 carbon

atoms, ether having from 4 to about 18 carbon atoms,

and hydroxyalkyl having from 1 to about 18 carbon

atoms; and

        R$_1$ and R$_2$ together, or R$_3$ and R$_4$ together, or

each pair, may be cyclized forming a ring having from

about 5 to about 14 carbon atoms.

        90. The process of claim 89 wherein said stable

free radical agent is selected from the group

consisting of 1-tertbutyl-3,3,5,5-tetramethyl-2-

piperazinone-oxide, 3-isobutyl-1-isopropyl-3,5,5-

trimethyl-2-piperazinone-oxide, 1-isopropyl-3-phenyl-

3,5,5-trimethyl-2-piperazinone-oxide, 3,3-

tetramethylene-5,5-dimethyl-1-isopropyl-2-

piperazinone-oxide, 3,3-pentamethylene-5,5-dimethyl-1-

isopropyl-2-piperazinone-oxide, 3,3-hexamethylene-5,5-

dimethyl-1-isopropyl-2-piperazinone-oxide, and bis-

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3,3,5,5-pentamethylene-2,6-piperazinone-dione-oxide.

91.   The process of claim 89 wherein said stable

free radical agent is selected from the group

consisting of 3,3,5,5-tetramethyl-2-morpholone-oxide,

3,3-pentamethylene-5,5-dimethyl-2-morpholone-oxide,

5   and 3,3-hexamethylene-5,5-dimethyl-2-morpholone oxide.

92.   The process of claim 89 wherein said free

radical agent is 3,3-hexamethylene-5,5-dimethyl-2-

morpholone oxide.

93.   The process of claim 89 wherein said

polymerizable monomer compound is selected from the

group consisting of styrene and derivatives thereof,

conjugated dienes and derivatives thereof, acrylates

5   and derivatives thereof, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C08F4/00   C08F2/38

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 412 047 A (M.K. GEORGES) 2 May 1995 cited in the application see claims 1,3 ---	1
A	WO 94 11412 A (XEROX) 26 May 1994 cited in the application -----	

☐ Further documents are listed in the continuation of box C.   ☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search	Date of mailing of the international search report
21 July 1998	05/08/1998

Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Cauwenberg, C

Form PCT/ISA/210 (second sheet) (July 1992)

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

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